



NRC Publications Archive Archives des publications du CNRC

Comparison of IR techniques for the characterization of construction cement minerals and hydrated products

Delgado, A. H.; Paroli, R. M.; Beaudoin, J. J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

Applied Spectroscopy, 50, 8, pp. 970-976, 1996

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=cb50a727-d24b-4903-bb49-dd0eba541ee1>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=cb50a727-d24b-4903-bb49-dd0eba541eeb>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





Comparison of IR techniques for the characterization of construction cement minerals and hydrated products

NRCC-39008

Delgado, A.H.; Paroli, R.M.; Beaudoin, J.J.

September 1996

A version of this document is published in / Une version de ce document se trouve dans:
Applied Spectroscopy, 50, (8), pp. 970-976, 1996

The material in this document is covered by the provisions of the Copyright Act, by Canadian laws, policies, regulations and international agreements. Such provisions serve to identify the information source and, in specific instances, to prohibit reproduction of materials without written permission. For more information visit <http://laws.justice.gc.ca/en/showtdm/cs/C-42>

Les renseignements dans ce document sont protégés par la Loi sur le droit d'auteur, par les lois, les politiques et les règlements du Canada et des accords internationaux. Ces dispositions permettent d'identifier la source de l'information et, dans certains cas, d'interdire la copie de documents sans permission écrite. Pour obtenir de plus amples renseignements : <http://lois.justice.gc.ca/fr/showtdm/cs/C-42>



National Research
Council Canada

Conseil national
de recherches Canada

Canada

Comparison of IR Techniques for the Characterization of Construction Cement Minerals and Hydrated Products

ANA. H. DELGADO, RALPH M. PAROLI,* and JAMES J. BEAUDOIN

Institute for Research in Construction, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

The influence of FT-IR sampling techniques on the characterization of cement systems was investigated. Three FT-IR techniques were used to study tricalcium silicate (C_3S), hydrated C_3S , calcium hydroxide, and calcium silicate hydrate (C-S-H). They include transmission spectroscopy (TS), photoacoustic spectroscopy (PAS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The TS technique (using KBr pellets) was the most labor-intensive but was found to give the simplest spectra with well-defined bands. The PAS technique was found to be the simplest technique but yielded bands at lower wavenumber than TS. DRIFTS was determined to be a good alternative for cement powders since it provided spectra similar to those for the TS technique. DRIFTS required more sample preparation than PAS but less sample preparation than the KBr pellet technique.

Index Headings: Portland cement; Tricalcium silicate (C_3S); Calcium silicate hydrate (C-S-H); Fourier transform infrared (FT-IR) spectroscopy; Transmission spectroscopy (TS); Diffuse reflectance spectroscopy (DRIFTS); Photoacoustic spectroscopy (PAS).

INTRODUCTION

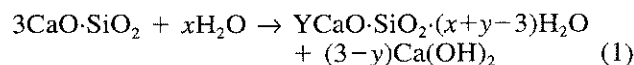
Investigation of existing buildings, or the testing of the materials from which they are constructed, constitutes a high proportion of work in the construction area. This area requires the availability of a wide range of testing techniques capable of providing detailed information on both the chemical and physical conditions of the constituent materials of the building structure. These techniques are needed to detect cracking, voids, corrosion, or other forms of degradation and to identify the reason for such problems. In most cases, these investigations involve existing residential and/or commercial buildings. Therefore, it is necessary to use nondestructive techniques to obtain quick and accurate information without causing damage to the finish and decoration of the structure. Hence, there is a continuous need for developing new analytical techniques or adapting existing ones.

Cement is one of the most common building materials in the construction industry. Ordinary Portland cement (OPC) is obtained by heating to approximately 1300–1450 °C a mixture of calcareous and argillaceous raw materials and grinding it. The calcareous materials, whose main constituent is calcium carbonate, include limestone, chalk, marlsea shells, etc. Magnesium and other alkaline earth carbonates also occur in considerable quantities in dolomitic and other low-grade limestones. The argillaceous materials, on the other hand, are mainly clays with a widely varying composition. Tricalcium silicate (C_3S) and β -dicalcium silicate (C_2S) are the important silicate minerals in Portland cement.¹ These two sil-

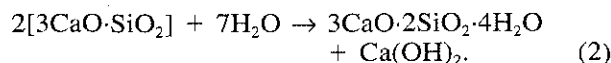
icates together make up 70–80% of the Portland cement.² However, the main component is tricalcium silicate ($3CaO \cdot SiO_2$),[†] which imparts strength. Gypsum or $C\bar{S}H_2$ ($CaSO_4 \cdot 2H_2O$) is added to cement in small amounts to control the setting properties of the cement. Portland cement, as ordinarily prepared, is a fine-grained multiphase material with four major phases. The phases are summarized in Table I.

Table I shows the complexity of the Portland cement material, which becomes even more complex upon hydration. Calcium silicate hydrate is formed upon hydration of alite (C_3S , which contains Fe, Al, Mg, Cr, and Zn) and belite (C_2S , where Ca is replaced by Na, Al, Mg, K, Cr, and Mn).³ The principal hydration products of OPC are calcium silicate hydrate (C-S-H), calcium hydroxide, ettringite, and/or the monosulphate/ C_4AH_{13} solid solution. To understand the complex reactions occurring during the hydration process of cement, it is important to know the hydration behavior of its individual components. For example, tricalcium silicate reacts with a limited amount of water and forms calcium silicate hydrates of given composition $C_xS_xH_x$ and $Ca(OH)_2$. Most of the hydration reaction occurs within a month. However, complete hydration occurs only after several years under normal curing conditions. In a fully hydrated C_3S paste, about 60–70% of the solid is C-S-H.²

The following reactions illustrate the basic hydration process of C_3S :²



generally represented as:



The amount of $Ca(OH)_2$ produced in the hydration of C_2S is less than in C_3S . The dicalcium silicate phase hydrates much more slowly than the tricalcium silicate phase. The stoichiometry of the above chemical reaction is not completely known, since it is difficult to estimate the composition of C/S and H/S ratios. According to Bensted,³ in the C-S-H gel-like solid formed upon hydration, the $CaO:SiO_2$ ratio is close to 1.5; however, depending on the nature of the cement, water/cement ratio, and temperature, this composition can change from 1.5 to 1.8.

Various analytical techniques have been used to study cement and its hydration products. They include thermal analysis (e.g., DTA),^{4–6} solid-state high-resolution ^{29}Si NMR, X-ray diffraction,^{7,8} infrared spectroscopy,^{3,4,5,8–17}

Received 24 April 1995; accepted 7 March 1996.

* Author to whom correspondence should be sent.

† Mineralogical notation is used in cement chemistry, i.e., C = CaO; S = SiO_2 ; H = H_2O ; \bar{S} = SO_3 .

TABLE I. Major phases present in Portland cement.^a

Tricalcium silicate (3CaO·SiO ₂)	C ₃ S (is a synthesized product).
Alite (or substituted C ₃ S)	C ₃ S which contains Fe, Al, Mg, Cr, and Zn. Once hydrated, will provide strength to cement.
Dicalcium silicate (2CaO·SiO ₂)	C ₂ S is primarily β-dicalcium.
Belite (or substituted C ₂ S)	C ₂ S where Ca is replaced by Na, Al, Mg, K, Cr, and Mn.
Tricalcium aluminate (3CaO·Al ₂ O ₃)	C ₃ A.
Ferrite 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	C ₄ AF is a solution of average composition from C ₂ F to C ₆ A ₂ F.
Other components	Sulfates resulting from the addition of 4% gypsum CaSO ₄ ·2H ₂ O (CSH ₂) to clinker during grinding.

^a See Refs. 2 and 3.

TABLE II. C-S-H preparations.^a

Sample	110	112	101	113	106	107
C/S	0.68	0.87	0.99	1.17	1.26	1.49
H/S	1.91	2.01	2.49	2.58	5.53	6.69

^a See Ref. 6.

scanning electron microscopy (SEM),^{11,13} Raman,^{4,16} and Fourier transform (FT)-Raman microspectroscopy.¹⁸

Infrared spectra in the transmission spectroscopy (TS) mode of cements and related materials have been obtained by using the traditional KBr or Nujol mull sampling techniques. Bensted and his co-worker^{3-4,10-13,16} have studied hydration behavior of cements using both the KBr pellet and Nujol mull techniques. Infrared spectra obtained of γ- and β-C₂S, C₃S, and the hydration products of the latter have been obtained by using the KBr and NaCl prism.⁹ Ramirez et al.¹⁷ have also used the pellet technique to study simulated corrosion of reinforcing steel in concrete by salt intrusion. In the last decade, new infrared sampling techniques, such as ATR, have been shown to be useful in the analysis of the cement of variable composition.¹⁵ Recently, Bonen et al.¹⁸ analyzed commercial and synthetic clinker minerals by Fourier transform infrared (FT-IR) and FT-Raman microspectroscopy. In spite of this, the KBr pellet and the Nujol mull techniques continue to be the most widely used. KBr pellet, however, is very time-consuming, and Nujol mull can obliterate crucial IR regions.

Specimen preparation can be reduced greatly by using other IR sampling techniques such as photoacoustic (PAS) or diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). These techniques not only provide spectral information similar to that obtained by TS but also reduce sample preparation and analysis time.

Because of the complexity of the OPC system, it is difficult to study the hydration process of individual components (the hydration reaction of one component may be hindered by another). For example, hydration of the tricalcium aluminate (C₃A) occurs very quickly, interfer-

ing with the hydration of C₃S. The latter, upon hydration, is responsible for strength; thus, it is important to isolate and understand the hydration process. This procedure is greatly facilitated through the use of pure calcium silicate hydrate in research investigations.

In this study, synthetic C₃S and calcium silicate hydrate (C-S-H) of different C/S and H/S compositions were prepared in the laboratory⁶ and studied by infrared spectroscopy with the use of different sampling techniques. Results obtained from FT-IR analysis of powdered synthetic C₃S, calcium hydroxide, and six C-S-H preparations with the use of three techniques—TS, PAS, and DRIFTS—are presented and compared.

EXPERIMENTAL

Synthetic C₃S and six synthetic calcium silicate hydrate preparations with a wide range of C/S and H/S ratios (supplied by Lafarge Coppee Recherche, France) were studied. Details of specimen preparation have been described elsewhere.⁶ Hydrated C₃S with a water/solid ratio of 0.5 was also studied. The C/S and H/S ratios of six C-S-H preparations are given in Table II. Powdered tricalcium silicate (C₃S), calcium hydroxide, and the six calcium silicate hydrate (C-S-H) preparations were analyzed by FT-IR spectroscopy using three sampling techniques: TS (KBr pellet), PAS, and DRIFTS. The analysis was performed with a Nicolet FT-IR (Model 800) connected to a Balston air dryer (Model 75-60).

KBr pellets were prepared as follows: We mixed 750 mg of KBr crystals, ground with 2 or 5 mg of sample. Approximately half of the KBr/sample mixture was transferred to a 13-mm-diameter die, placed under vacuum in a RIIK 25-ton ring press for 10 min. The mixture was pressed under vacuum with a load of 10 tons for 2 min, released, pressed to 10 tons for 30 s, released, and pressed again for 30 s.

The photoacoustic spectra were obtained with an MTEC photoacoustic cell (Model 200). Samples were analyzed without any sample preparation, except for slight

TABLE III. Experimental parameters for the FT-IR analysis.

Parameters	Techniques		
	Transmission (KBr pellet)	Diffuse reflectance (DRIFTS) (SH003 option)	Photoacoustic (PAS)
Detector	DTGS	Photoacoustic	Photoacoustic
Number of scans	32	128	128
Resolution	4 cm ⁻¹	4 cm ⁻¹	8 cm ⁻¹
Background	KBr pellet	KBr Powder	MTEC carbon black standard reference membrane
Mirror setting (velocity)	30 (0.63 cm/s)	10 (0.16 cm/s)	20 (0.32 cm/s)
Purge gas	Dry air	Helium (5 mL/s)	Helium (5 mL/s)

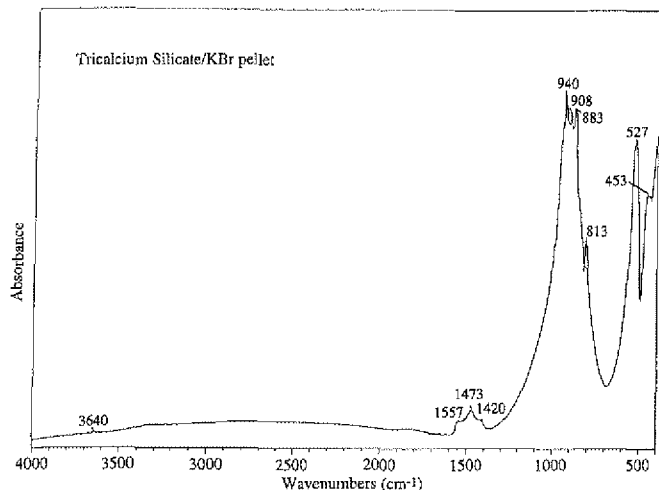


FIG. 1. Infrared spectrum of tricalcium silicate obtained by TS.

grinding of the hydrated C_3S . Powdered samples were placed in a 10-mm-diameter stainless steel pan and scanned. The background was scanned with the use of a carbon black standard reference membrane under the same conditions as the sample. Helium was used as a purge gas at a flow rate of 5 mL/s.

The diffuse reflectance spectra were obtained with the DRIFTS sample head option SH003 on the MTEC Model 200 photoacoustic cell. Samples were diluted to approximately 1% by weight with KBr crystals and ground to a powder for about a minute. All spectra were ratioed against a background obtained from pure ground KBr scanned the same day. Helium gas (5 mL/s) was used to purge the sample.

Experimental parameters used with each FT-IR technique are summarized in Table III. The DRIFTS spectra were converted to Kubelka-Munk units by using the KLB routine from the SX Nicolet software. The automatic or manual baseline-correction/normalize routines from the OMNIC software (Nicolet Instruments) were used to correct the baseline of the spectra before plotting. All stack spectra were normalized before plotting.

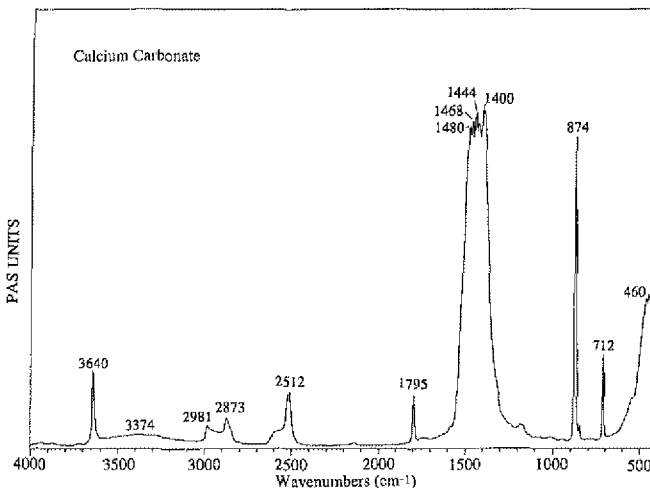


FIG. 3. Infrared spectrum of calcium carbonate obtained by PAS.

RESULTS AND DISCUSSION

The infrared absorption spectrum of C_3S obtained by using the KBr pellet technique is displayed in Fig. 1. The spectrum shows a strong broad band in the 1200–800- cm^{-1} region, with maxima at 940, 908, and 883 cm^{-1} , and two sharp bands at 813 and 527 cm^{-1} . The bands in the 1200–800- cm^{-1} region and that at 813 cm^{-1} can be attributed to the antisymmetrical and symmetrical stretching vibrations of SiO_4 , respectively, whereas the band at 527 cm^{-1} is ascribed to the out-of-plane bending vibrations of SiO_4 . The bands below 500 cm^{-1} are due to the in-plane bending vibration of SiO_4 . Such bands are typical for anhydrous tricalcium silicate.^{1,3} The spectrum also shows a broad and unresolved band between 1600 and 1400 cm^{-1} and another weak one at ~ 3640 cm^{-1} . The latter can hardly be seen, because of the scale used. These bands do not result from any pure C_3S vibrations. The band at 3640 cm^{-1} is typical of free OH groups. This observation suggests that the C_3S may have been partially hydrated. The 3640- cm^{-1} band is useful for diagnosis of the initiation of the hydration process.³ It has also been

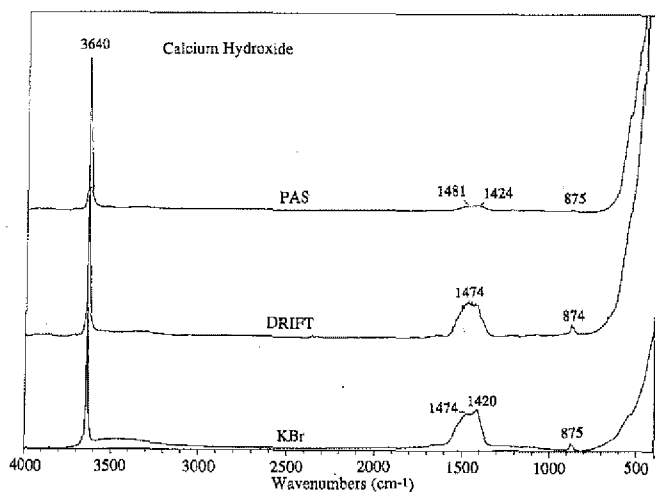


FIG. 2. Infrared spectrum of calcium hydroxide obtained by TS, DRIFTS, and PAS techniques.

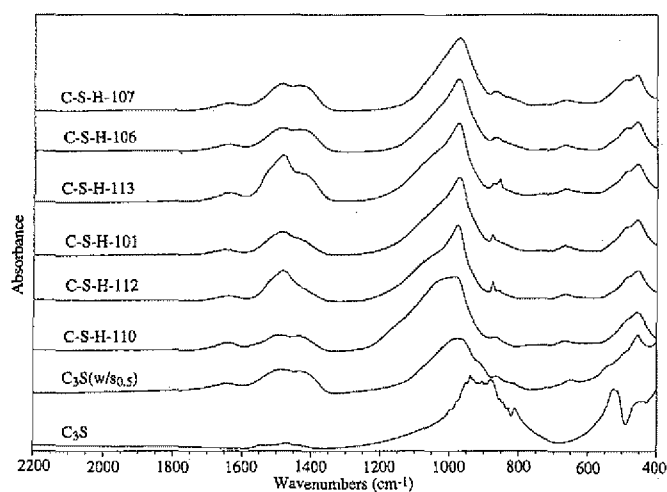


FIG. 4. Infrared spectra of cement preparations obtained by TS in the 2200–400- cm^{-1} region.

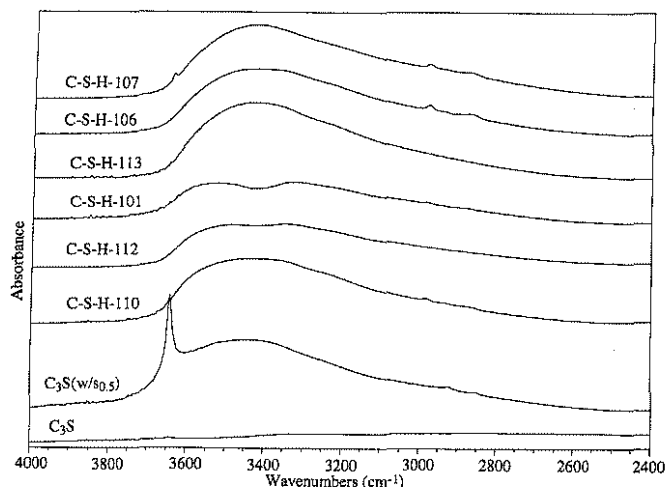


FIG. 5. Infrared spectra of cement preparations obtained by TS in the 4000–2400-cm⁻¹ region.

reported¹⁵ that splitting of the band in the 1000–850-cm⁻¹ region results from the presence of silicate phases. Since calcium hydroxide is one of the hydration products of Portland cement and C₃S, the calcium hydroxide spectrum shown in Fig. 2 was obtained by three different sampling techniques. Spectra show bands at 3640 cm⁻¹ and between 1600 and 1400 cm⁻¹ that are similar to those observed in the C₃S. The spectra obtained by the KBr technique and by PAS show an unresolved broad band with two maxima (~1480 and 1420 cm⁻¹) in the same spectral range as those at 1473 and 1420 cm⁻¹ observed in Fig. 1. Therefore, the bands between 1600 and 1400 cm⁻¹ are likely to be due to hydration of C₃S. The band maximum may differ slightly from spectrum to spectrum, depending on the broadness of the band. Pressure applied during the KBr pellet preparation, as well as particle size, can affect the band shape (Christiansen effect).

Atmospheric CO₂ attacks some compounds in cements and its hydration products.³ Exposure of cement to CO₂

TABLE IV. IR bands (cm⁻¹) for C₃S and C₃S(w/s_{0,s}) by KBr, DRIFTS and PAS techniques.^a

C ₃ S			C ₃ S(w/s _{0,s})		
KBr	DRIFTS	PAS	KBr	DRIFTS	PAS
3640 vw		3642 vw	3644 s 3446 m,b	3644 m	3641 m
		1806 w,b			3364 m,b
			1653 w	1650 w,b	1643 w
1557 w					
1473 w	1473 w	1480 w	14880 m	1479 m,b	1479 m
1420 w		1420 w	1436 sh		1424 m
				1387	
	995 sh				
940 vs	938 vs	935 s	972 vs	965 vs	958 vs
908 m					
883 s	884 s	880 vs	866 sh	866 sh	861 sh
	856 sh	855 sh			
	816 m	814 m			
	668 w		651 w	668 w	652 w
527 s	522 s	518 s			
453 sh	454 sh	450 s	453 s	456 s	453 s
	440 sh	438 s			

^a Note: vw = very weak; s = strong; m = medium; b = broad; w = weak; sh = shoulder; vs = very strong; s = strong.

TABLE V. IR bands (cm⁻¹) for 110 and 112 by KBr, DRIFTS and PAS techniques.^a

110			112		
KBr	DRIFTS	PAS	KBr	DRIFTS	PAS
		3740 w			3743 vw
3441 m,b		3425 mw	3483 m,b		
	3356 m,b		3347 m,b	3402 m,b	3436 m,b
1646 w	1636 w	1635 w	1637 w	1635 w	1634 w
1490 m	1490 m	1489 m	1483 m	1483 m	1474 m
1436 m	1437 m	1429 m			
982 vs	978 vs	979 vs	974 vs	972 vs	964 vs
868 sh	867 sh	865 sh	876 m	876 m	875 m
667 w	668 w	664 w	667 w	668 w	667 w
456 s	457 s	448 s	454 s	445 s	450 s

^a Note: w = weak; vw = very weak; m = medium; b = broad; mw = medium weak; vs = very strong; s = strong.

results very quickly in carbonation. The calcium carbonate spectrum (shown in Fig. 3) was obtained by the PAS technique to determine whether the cement had carbonated. The strong bands in the 1600–1300-cm⁻¹ region and at 874 cm⁻¹ observed in the spectrum are due to the anti-symmetrical stretch and out-of-plane bending of the C–O, respectively, and the medium intensity one at 712 cm⁻¹ is due to the angular bending of the O–C–O.³ The medium band at 2512 cm⁻¹ may be a combination of the 874- and 1400-cm⁻¹ bands, and that at 1795 cm⁻¹ is probably an overtone of the 874-cm⁻¹ band. However, in minerals containing hydroxyl ions, the carbonate bands may be displaced to a higher wavenumber.¹ The spectrum also shows the presence of free OH groups at 3640 cm⁻¹, which can be due to calcium hydroxide impurities; a weak broad band at 3374 cm⁻¹, typical of bonded OH; and bands at 2981 and 2873 cm⁻¹, which may be overtones and combinations of the bands centered at 1444 cm⁻¹. With the exception of the bands at 3640 cm⁻¹ and in the 1600–1300-cm⁻¹ region, no other carbonate bands are observed in the C₃S spectrum.

A comparison of the spectrum of Ca(OH)₂ and CaCO₃ with that of C₃S suggests that the latter has undergone mainly hydration rather than carbonation. A level of 1% carbonate in silicates can be easily detected in the 1600–1400-cm⁻¹ region.¹

TABLE VI. IR bands (cm⁻¹) for 101 and 113 by KBr, DRIFTS and PAS techniques.^a

101			113		
KBr	DRIFTS	PAS	KBr	DRIFTS	PAS
		3742 vw			3740 vw
3527 m,b					
	3441 m,b	3433 m,b	3432 m,b		3402 m,b
3323 m,b	3360 m,b			3363 m,b	
				1789 vw	1789 vw
1652 w	1653 w	1635 w	1635 w	1636 w	1637 w
1488 m	1474 m	1474 m	1481 s	1482 s	1476 s
			1437 sh	1427 sh	1423 sh
971 vs	969 vs	959 vs	973 vs	969 vs	962 vs
875 m	875 m	874 m	874 sh	874 sh	867 sh
			856 m	856 m	850 m
668 w	668 w	667 w	667 w	668 w	665 w
	480		489 sh	482 sh	481 sh
455 s	457 s	439 s	455 s	448 s	447 s

^a Note: vw = very weak; m = medium; b = broad; w = weak; s = strong; sh = shoulder; vs = very strong.

TABLE VII. IR bands (cm^{-1}) for 106 and 107 by KBr, DRIFTS and PAS techniques.^a

106			107		
KBr	DRIFTS	PAS	KBr	DRIFTS	PAS
			3642 vw		
	3532 m,b			3543 m,b	
3426 m,b	3459 m,b		3429 m,b		
	3337 m,b	3391 w,b		3319 m,b	3378 w,b
				3047 vw,b	
2979 vw	2978 vw	2977 vw	2979 vw	2978 vw	2977 vw
2875 vw	2870 vw	2866 vw	2867 vw	2869 vw	2872 vw
1636 w	1636 w	1643 w	1640 w	1658 w	1641 w
1486 m	1483 m	1473 m	1485 m	1489 m	1474 m
1424 m	1426 m	1418 m	1425 m	1427 m	1418 m
	138 sh			1386 sh	
		1112 w			
971 vs	968 vs	958 vs	971 vs	962 vs	955 vs
865 w	865 m	860 m	866 w	862 w	860 w
667 w	668 m	663 w	671 w	668 w	660 w
491 sh	489 sh	482 sh	505 sh	492 sh	483 sh
456 s	451 s	446 s	466 s	453 s	446 s
			458		

^a Note: vw = very weak; m = medium; b = broad; w = weak; sh = shoulder; vs = very strong; s = strong.

A general overview of the cement spectra, from 2200 to 400 cm^{-1} obtained by TS and the use of the KBr pellet technique, is displayed in Fig. 4. The spectra show that, as the C/S ratio increases, the broad band at $\sim 940 \text{ cm}^{-1}$ due to stretching vibration of the SiO_4 not only becomes narrower but also shifts to higher wavenumber. In addition, a weak band in the 1600–1500- cm^{-1} region starts to appear, whereas the 500- cm^{-1} band almost disappears. Figure 5 displays the 4000–2400- cm^{-1} region for the spectra shown in Fig. 4. As can be observed, the free OH band in the hydrated C_3S spectrum with a water/solid ratio of 0.5 is more intense than in other spectra. The DRIFTS and PAS spectra displayed a similar trend in both regions. In general, the spectra obtained by the three different sampling techniques do not differ greatly from one sampling technique to another. This result suggests that either technique can be used to study the hydration of cement. It is important to note that almost all spectra, regardless of the sampling technique used, show bands

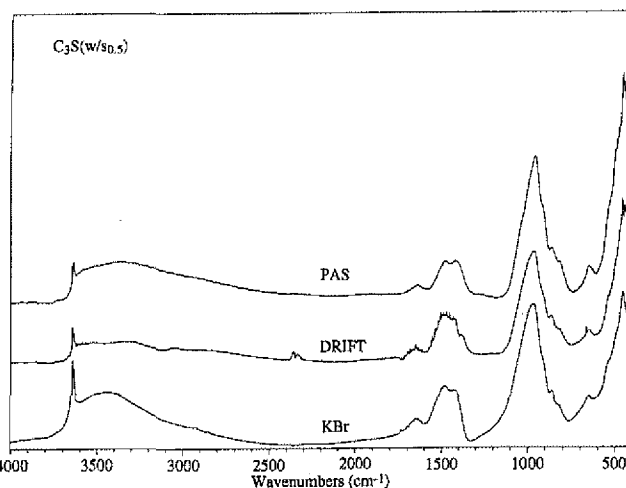


Fig. 7. Infrared spectrum of hydrated tricalcium silicate with a water/solid ratio of 0.5 obtained by TS, DRIFTS, and PAS techniques.

between 2900 and 2800 cm^{-1} . Such bands may result from the solvents used to dry the preparations.

The spectra for each preparation obtained by the three sampling techniques used in this study are shown in Figs. 6–13. The positions of the IR bands for the preparations studied are summarized, with respect to sampling techniques, in Tables IV–VII. Each table contains two preparations with C–S–H samples given by increasing C/S ratios.

The spectral features for the C_3S sample present in the TS spectrum (Fig. 6) are similar to those present in the DRIFTS and PAS spectra. Similarly, the spectrum for the hydrated tricalcium silicate with a water/solid ratio of 0.5 [$\text{C}_3\text{S}(w/s_{0.5})$], displayed in Fig. 7, shows similar spectral bands, regardless of the sampling technique used to collect the spectrum. The shifting of the band at $\sim 940 \text{ cm}^{-1}$ in the anhydrous C_3S (Fig. 6), to $\sim 970 \text{ cm}^{-1}$ for TS and DRIFTS, and to $\sim 960 \text{ cm}^{-1}$ for PAS in the $\text{C}_3\text{S}(w/s_{0.5})$ spectrum is an indication of hydration of the tricalcium silicate. Shpynova et al.¹⁹ reported that, after 15 years of hydration, the 938- cm^{-1} band that they observed in the anhydrous C_3S gradually shifted to 989 cm^{-1} , whereas

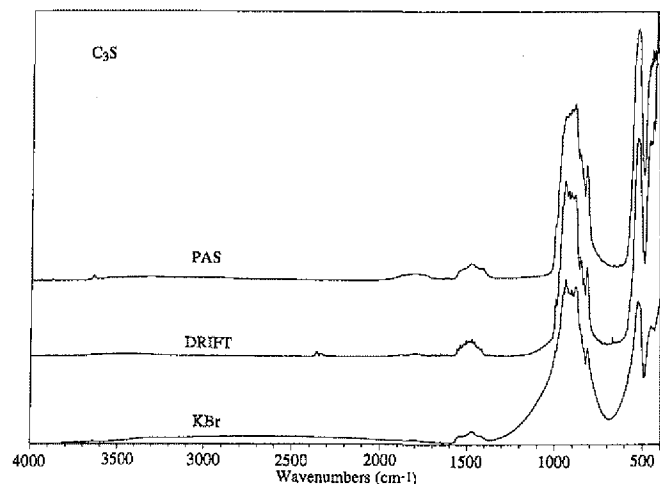


Fig. 6. Infrared spectrum of tricalcium silicate obtained by TS, DRIFTS, and PAS techniques.

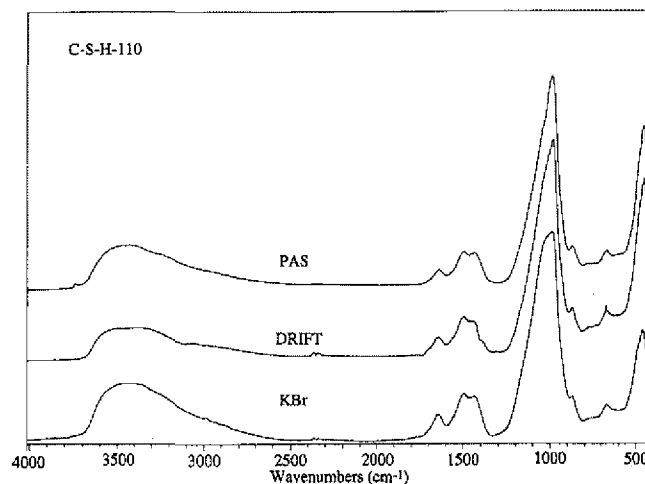


Fig. 8. Infrared spectrum of C–S–H–110 obtained by TS, DRIFTS, and PAS techniques.

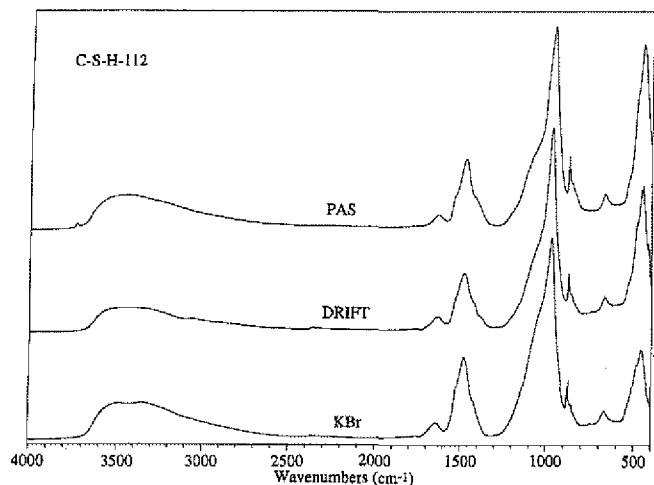


FIG. 9. Infrared spectrum of C-S-H-112 obtained by TS, DRIFTS, and PAS techniques.

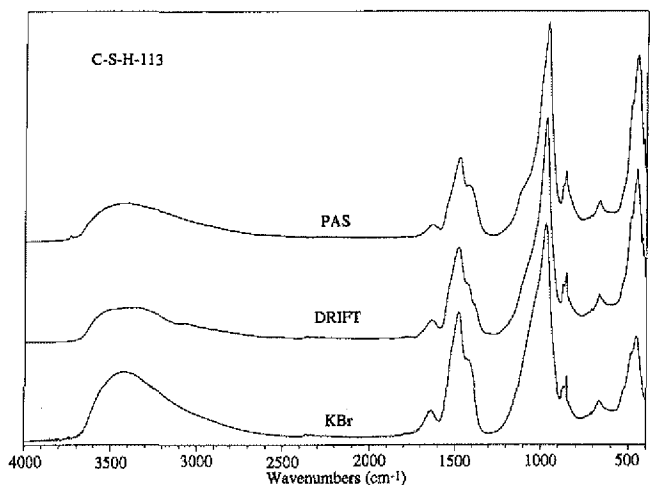


FIG. 11. Infrared spectrum of C-S-H-113 obtained by TS, DRIFTS, and PAS techniques.

the band at 878 cm^{-1} remained unaffected. A similar shift was also observed by Bensted and Varma.²⁰ Other spectral bands observed in Fig. 7 are the free OH stretching absorption bands at $\sim 3640\text{ cm}^{-1}$ resulting from the calcium hydroxide; the broad band in the $3500\text{--}3200\text{-cm}^{-1}$ region from the OH stretching vibrations of the C-S-H; and a weak broad band at $\sim 1650\text{ cm}^{-1}$, which may be assigned to the water bending vibrations.³ The shifting of the 940-cm^{-1} band to higher wavenumber in the C-S-H suggests the possibility of continuous changes in the C_3S structure as hydration takes places. Hence, a more compact and highly condensed framework may form, resulting in changes in molecular interactions. Another indication of hydration is the 500-cm^{-1} band observed in Fig. 6, which is noticeably absent in Fig. 7. The chemical environment of the bending vibrations of the bonds changes as hydration occurs. This factor is probably responsible for the appearance of a well-defined band at $\sim 460\text{ cm}^{-1}$. Bensted³ has reported that IR bands below 600 cm^{-1} observed in the C-S-H spectrum are wide and flattened, indicating poor crystallinity; such bands are not suitable for characterization purposes. In addition, he re-

ported that broad bands in the C-S-H spectrum are consistent with the presence of poorly crystalline, nonstoichiometric, gel-like solid.

The infrared spectra obtained by using the KBr pellet technique (TS), DRIFTS, and PAS for preparations with C/S ratios of 0.68 (C-S-H-110) and 0.87 (C-S-H-112), respectively, are displayed in Figs. 8 and 9. In general, the IR bands observed for the two preparations show bands similar to those observed in Fig. 7, with the exception of the band at $\sim 660\text{ cm}^{-1}$, which is absent in the previous spectrum. The sharp peak superimposed in the DRIFTS spectrum at $\sim 670\text{ cm}^{-1}$ can be attributed to atmospheric CO_2 , as was observed by Ghosh and Chatterjee¹⁵ during the analysis of Portland cement by attenuated total reflectance (ATR). They attributed this band to atmospheric CO_2 . The main band at $\sim 660\text{ cm}^{-1}$ can, however, be attributed to the Si-O-Si symmetric vibrations.¹⁸

Figures 10-13 display the spectra for the remaining four preparations studied. Once again, IR bands for the different preparations obtained by TS are also observed in the DRIFTS and PAS spectra. Generally, the bands in

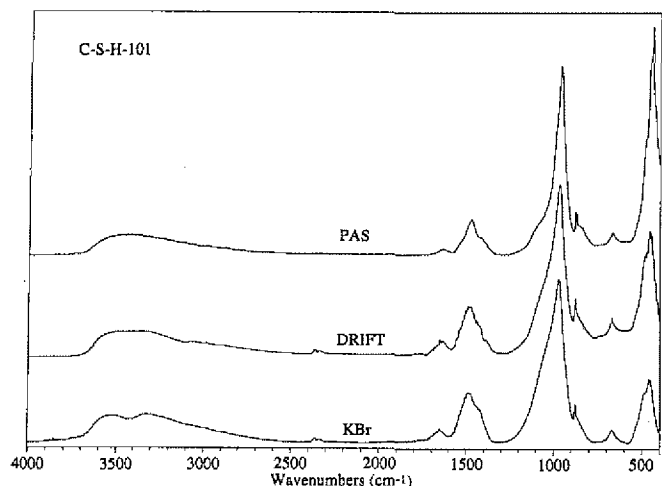


FIG. 10. Infrared spectrum of C-S-H-101 obtained by TS, DRIFTS, and PAS techniques.

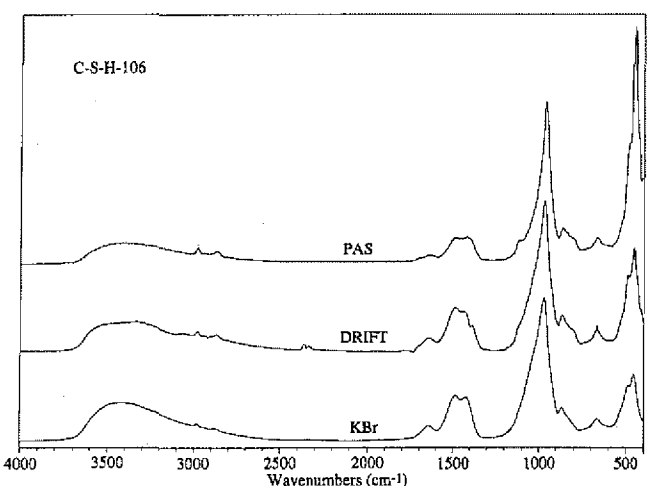


FIG. 12. Infrared spectrum of C-S-H-106 obtained by TS, DRIFTS, and PAS techniques.

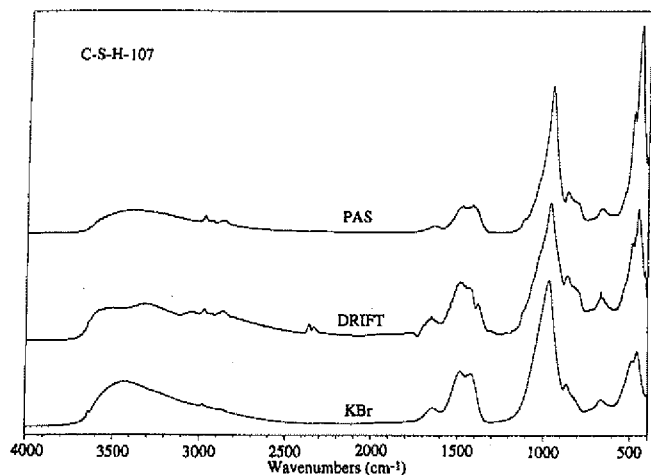


FIG. 13. Infrared spectrum of C-S-H-107 obtained by TS, DRIFTS, and PAS techniques.

the PAS spectra seem to appear at a slightly lower wavenumber than those in the TS and DRIFTS spectra.

CONCLUSION

The IR spectra obtained by the TS technique are simpler and have better-defined bands than those obtained by either the DRIFTS or the PAS technique. However, the TS technique is very labor-intensive. The results suggest that DRIFTS is a good alternative for powdered samples such as cement, even though it gave slightly noisier spectra than the other two. It requires less sample preparation than the TS technique. The PAS technique was found to be the easiest technique of the three, since it requires hardly any sample preparation. The IR bands of the spectra obtained by this technique appeared at slightly lower wavenumber than those in TS and DRIFTS.

A comparison of the spectra obtained by the three FT-IR techniques leads to the conclusion that, although some small differences are observed in the spectra, any of the three techniques can be used to study cement and the associated hydration products. PAS was the easiest technique. PAS bands were found to occur at lower wavenumber than those from the KBr pellet and DRIFTS techniques. DRIFTS was found to be a good alternative for cement powders. DRIFTS requires more sample preparation than PAS but much less than the KBr pellet technique.

The following conclusions may be drawn from the re-

sults of this study: The 3640-cm^{-1} band contains OH stretching vibrations of $\text{Ca}(\text{OH})_2$. The 3450-cm^{-1} band is attributed to OH stretching vibrations of the C-S-H. The $1700\text{-}1500\text{-cm}^{-1}$ band corresponds to the bending of the OH groups in the C-S-H and may be representative of hydrated samples. The $1200\text{-}800\text{-cm}^{-1}$ region is attributed to the stretching vibrations of SiO_4 , and the $500\text{-}400\text{-cm}^{-1}$ region is associated with the bending vibration of SiO_4 .

ACKNOWLEDGMENTS

The authors are grateful Mr. Bob Myers for preparing the cement mixtures and to Ms. Genevieve Sauvé for her assistance in acquiring some of the data presented in this paper.

1. *Infrared Spectroscopy for Characterization and Evaluation of Cements and Related Materials* (Cement Research Institute of India, New Delhi, RB-6-76, 1976), pp. 1-48.
2. V. S. Ramachandran and R. F. Feldman, "Cement Science", in *Concrete Admixtures Handbook: Properties, Science, and Technology*, V. S. Ramachandran, Ed. (Noyes Publications, Park Ridge, New Jersey, 1984), Chap. 1.
3. J. Bensted, "Applications of Infrared Spectroscopy to Cement Hydration", paper delivered at the Construction Materials Group and Institute of Materials Meeting on Techniques for Characterization of Cement Hydration, London (1994) (Society of Chemical Industry).
4. J. Bensted and S. P. Varma, *Cement Technol.* **5**, 440 (1974).
5. J. Bensted, *World Cement Technol.* **11**, 395 (1980).
6. J. J. Beaudoin, V. S. Ramachandran, and R. F. Feldman, *Cement and Concrete Res.* **20**, 875 (1990).
7. G. M. M. Bell, J. Bensted, F. P. Glasser, E. E. Lachowski, D. R. Roberts, and M. J. Taylor, *Adv. Cement Res.* **3**, 23 (1990).
8. J. D. Ortego, Y. Barroeta, F. K. Cartiedge, and H. Akhter, *Environ. Sci. Technol.* **25**, 1171 (1991).
9. Ch. M. Hunt, "Chemistry of Cement", in *Proceeding of the Fourth International Symposium* Monograph 43 (United States Department of Commerce, National Bureau of Standards, Washington, D.C. Vol. 1, 1962), p. 297.
10. J. Bensted, *World Cement Technol.* **10**, 404 (1979).
11. J. Bensted, *World Cement Technol.* **8**, 171 (1977).
12. J. Bensted, *World Cement Technol.* **13**, 117 (1982).
13. J. Bensted, *World Cement Technol.* **13**, 85 (1982).
14. J. Bensted, *Il Cemento* **87**, 137 (1993).
15. S. N. Ghosh and A. K. Chatterjee, *J. Mat. Sci. Lett.* **10**, 1454 (1975).
16. J. Bensted and S. P. Varma, *Cement Technol.* **5**, 256 (1974).
17. C. W. Ramirez, B. Borgard, D. Jones, and R. C. Heidersbach, *Mat. Performance* **December**, 33 (1990).
18. D. Bonen, T. J. Johnson, and S. L. Sarkar, Preprint: *Cement and Concrete Res.* **24**, 959 (1994).
19. L. G. Shpynova, V. I. Sinen'kaya, V. I. Chikh, and I. I. Nikonets, "Formation of $\beta\text{-C}_2\text{S}$ and C_3S Cement Stone Microstructure", paper delivered at the VI International Congress on the Chemistry of Cement, Moscow (1974).
20. J. Bensted and S. P. Varma, *Cement Technol.* **5**, 378 (1974).